JUMO Analytical Measurement

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Information on pH measurement

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Information on pH measurement

1 Preface

The pH value is the most frequently used process variable in analysis. The pH value is of outstanding importance in water and environmental analysis and in almost all sectors of industry. Whether the cheese in a dairy is of the right quality, the water in a drinking water supply causes corrosion damage, or the precipitation in a treatment plant for waste water from an electroplating process occurs at the optimal point, all depend on such parameters as the pH value.

This technical publication presents the basic electrochemical relationships and typical applications in a general, easily understood form. In addition, information is provided on the current state of technology with regard to transmitters/controllers and sensors for this process variable.

We try to ensure that the “Information on pH measurement” is always kept fully up to date, and therefore appeal to our readers for feedback and the sharing of experience and knowledge. Any suggestions or contributions to the discussion will be most welcome.

Fulda, May 2003

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M.K. Juchheim, Fulda, Germany, May 2003

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2 Basics

2.1 General

pH is derived from the Latin pondus hydrogenii (weight of hydrogen) or potentia hydrogenii (effectiveness of the hydrogen).

Hydrogen ions

So the pH value concerns hydrogen, or more precisely hydrogen ions[1]. Hydrogen ions occur in water and aqueous solutions as a result of the dissociation of acid or water molecules.

Pure water dissociates (splits) into hydrogen ions (H^+) and hydroxide ions (OH^-).

$$H_2O \longrightarrow H^+ + OH^-$$

At room temperature, the minute quantity of 10^{-7} mol/l of hydrogen ions is present, corresponding to 0.0000001 g in one liter of water.

An acid contains much larger quantities of hydrogen ions. The hydrogen chloride molecule in hydrochloric acid dissociates 100 percent into hydrogen ions and chloride ions (Cl^-).

$$HCl \longrightarrow H^+ + Cl^-$$

Hydrochloric acid (HCl) with a concentration of $c_{(HCl)}$ = 1 mol/l contains 1 g/l hydrogen ions, that is 10 million times more than pure water.

The presence of dissolved alkalis also affects the quantity of the hydrogen ions in the aqueous solution. Sodium hydroxide in caustic soda (NaOH) splits almost 100 percent into sodium (Na^+) and hydroxide ions.

$$NaOH \longrightarrow Na^+ + OH^-$$

The more hydroxide ions are present, the smaller is the proportion of dissociated water molecules. Caustic soda with a concentration $c_{(NaOH)}$ = 1 mol/l contains 0.00000000000001 g/l hydrogen ions, that is 10 million times less than pure water, but the hydroxide ion concentration is 10 million times larger.

The more hydrogen or hydroxide ions a solution contains, the more aggressively it reacts.

1 It has been known since 1924 that hydrogen ions do not exist in aqueous solutions. The real causes of pH are oxonium and hydronium ions. However, the term “hydrogen ions” is so widespread that it is normally used instead of the terms “oxonium ions” or “hydronium ions”.

Information on pH measurement

pH value

The figures for the hydrogen ion concentration are very impractical and confusing. Sörensen simplified this by introducing the concept of pH in 1909. He simply used the negative value of the common logarithm (base 10) of the hydrogen ion concentration.

Hydrogen ion concentration	Exponential representation	pH value
0. 000 000 000 001 mol/l	10^{-12} mol/l	12
0. 000 000 1 mol/l	10^{-7} mol/l	7
1 mol/l	10^{0} mol/l	0

pH scale

The pH values of aqueous solutions can be arranged in a pH scale.

This scale ranges from strongly acidic to strongly basic (alkaline) solutions.

Acidic

Solutions with a pH value less than 7 are acidic; they contain more hydrogen ions than hydroxide ions.

Neutral

Solutions with a pH value of 7[2] are neutral; they contain equal quantities of hydrogen and hydroxide ions.

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Basic

Solutions with a pH value more than 7 are basic (alkaline); they contain less hydrogen ions than hydroxide ions.

Activity

The effect of the hydrogen ions does not depend on their concentration but on their activity. Solutions with the same hydrogen ion concentration can have different levels of aggressiveness.
The reason for this is the mutual interference of all the ions dissolved in the solution. For example, sulfate ions in sulfuric acid affect hydrogen ions differently from nitrate ions in nitric acid.
A chloride concentration $c_{(Cl^-)}$ = 100 g/l affects the hydrogen ions more strongly than a chloride concentration of $c_{(Cl^-)}$ =1 g/l. The valid definition of the pH used today no longer refers to the concentration of the hydrogen ions, but instead to their activity.

Definition

"pH is defined as the common logarithm of the molar hydrogen ion activity a^H, multiplied by (-1), divided by the unit of the molality m^0 = 1 mol kg^{-1}".

This definition is valid for hydrogen ion activities from 10^0 to 10^{-14} mol/l, that is for a range from pH = 0 to pH = 14.

---

[2] The precise neutral point depends on the temperature.

2.2 Electrochemical pH measurement

The pH value can be measured in a number of very different ways: colorimetric, photometric or electrochemical (see Chapter 6). When choosing a method, it is well known that the pH value is one of those process variables where the measurement result depends on the measurement method used. Different measurement methods can lead to different measurement results that are, in principle, all correct. To avoid any confusion arising as a result of this, national and international standards stipulate that the pH value must be measured electrochemically with a glass electrode. As a result, the electrochemical measurement principle is the basis of all standardized methods of pH measurement. There has only been a globally valid agreement for the pH value since 1999 (IUPAC, Provisional Recommendations). This was made possible when England gave up its own pH scale in favor of the Bates-Guggenheim convention used in every other country. Until then, Ireland and many Asiatic countries had used the English pH scale.

2.2.1 pH measurement electrodes

The sensor for the measurement is the pH electrode system. It consists of two electrochemical half-cells, the measuring electrode and the reference electrode. At the measuring electrode, hydrogen ions establish a potential that depends on the pH value of the measured solution. The potential of the reference electrode is unaffected by the pH value and remains constant. The difference between the two potentials determines the electrical signal of the sensor, it is the electrode system voltage.

Measuring circuit

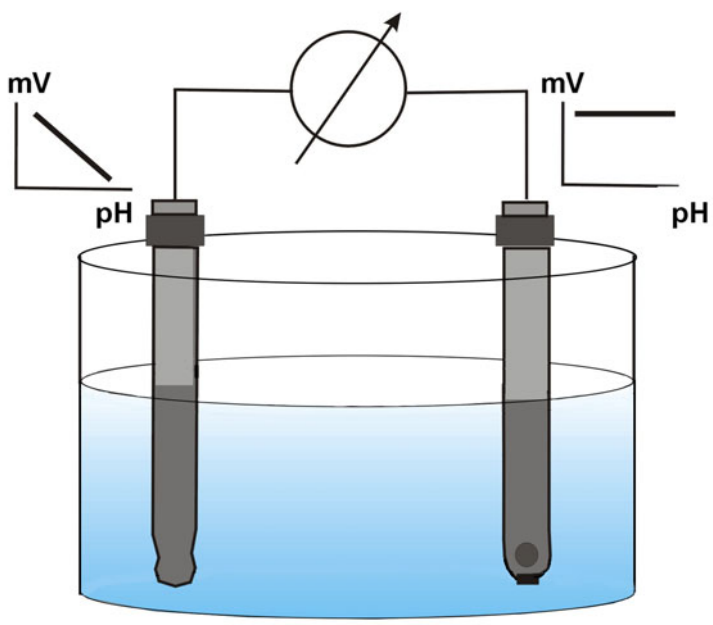

Fig. Arrangement of the pH measuring circuit

The pH measurement is made:

❏ with a glass electrode (measuring electrode) with a pH-sensitive membrane

glass and a reference electrode with a potential that is as independent as possible of pH and temperature,

❏ or with a combination electrode (glass and reference electrodes combined in a single assembly).

In practice, these two electrodes are incorporated in a more convenient combination electrode.

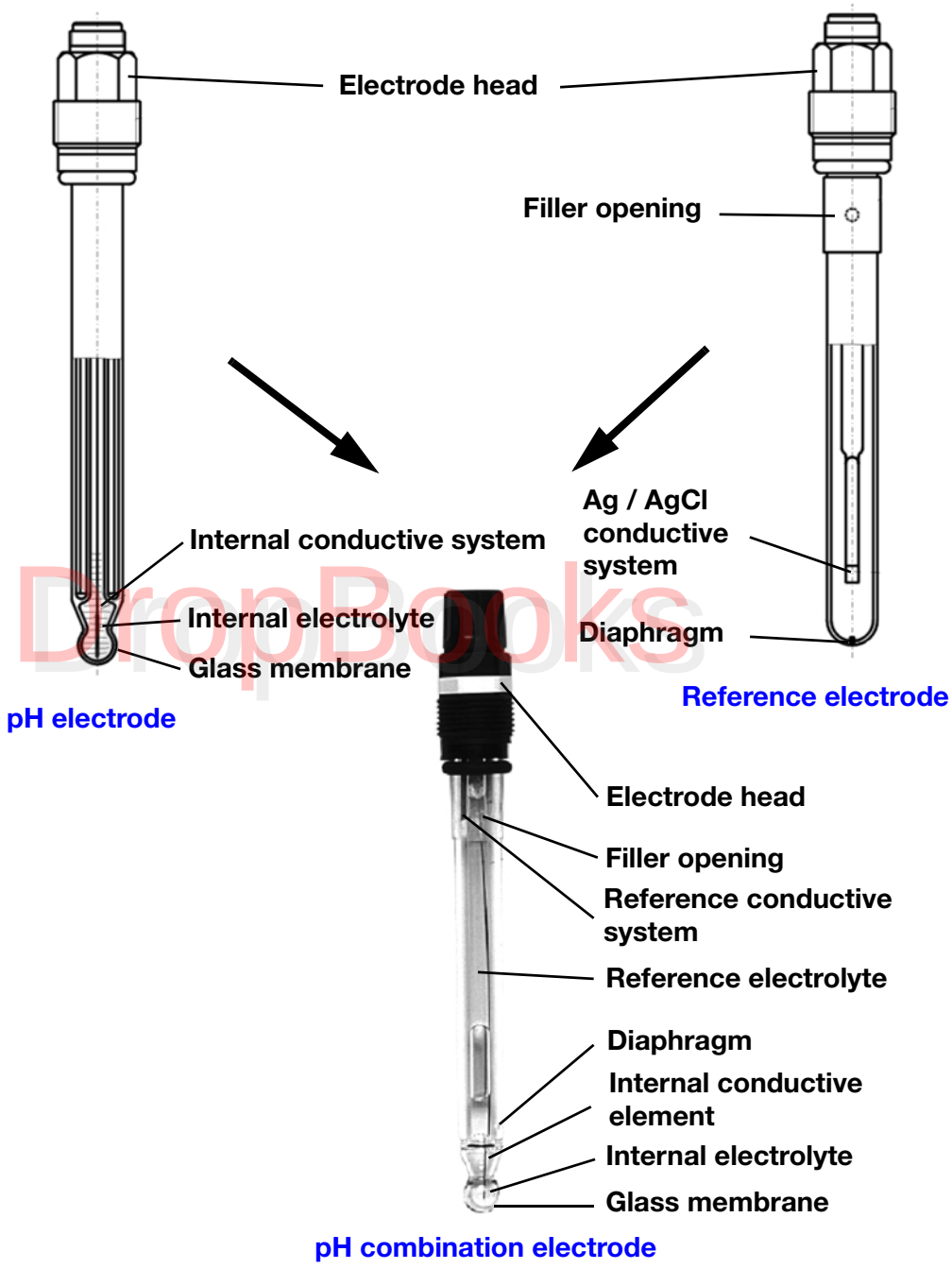

Fig. pH electrodes

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Information on pH measurement

Nernst equation

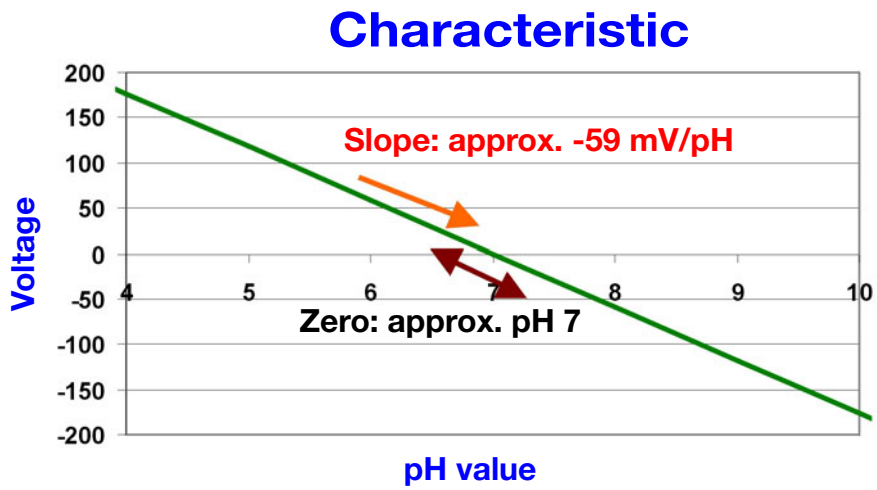

Fig. Characteristic of a pH electrode system

The relationship between pH and voltage is described by the Nernst equation:

$$\Delta E = E_0 - \frac{R \bullet T}{n \bullet F} \bullet \ln \frac{a_2}{a_1}$$

ΔE	electrode system voltage
E_0	standard voltage of the reference electrode
R	universal gas constant
T	absolute temperature
n	valency number of the hydrogen ions: n = 1
F	Faraday constant
a_1	activity of the hydrogen ions in the measured solution
a_2	activity of the hydrogen ions in the internal buffer (constant)

In practice, the expression $\frac{R \bullet T \bullet 2.303}{F}$ is called the Nernst voltage (k) and represents the theoretical slope of a pH electrode system.
At a temperature of 25°C, this corresponds to a voltage change of -0.059 V or -59 mV per logarithm to the base ten (pH unit).

Substituting this in the Nernst equation and then summarizing gives the following equation:

$$\Delta E = k' \bullet (pH - pH_0)$$

pH	pH of the measured solution
pH_0	pH coordinates of the system zero
k´	actual slope (determined during the calibration)

The system zero corresponds to the pH at which electrode voltage E = 0 mV.

Information on pH measurement

There are a number of different styles of measuring and reference electrodes.

pH electrode

The glass electrode is the most effective sensor for the measurement of pH. Its working range covers practically the entire pH range. Special membrane glasses are only required for strong alkaline solutions. The glass electrode has good reliability, and pH electrodes can last for several years and be used in most measured media. Modern styles are so robust that, for most applications, the fragility of glass, which often concerns users, does not present a problem.

How does the potential arise at the glass electrode?

The pH-sensitive element is the membrane, a rounded tip at the bottom end of the pH electrode. The membrane consists of a special silicate glass. When a glass membrane is ready for use, hydrogen ions are bound to its surface.

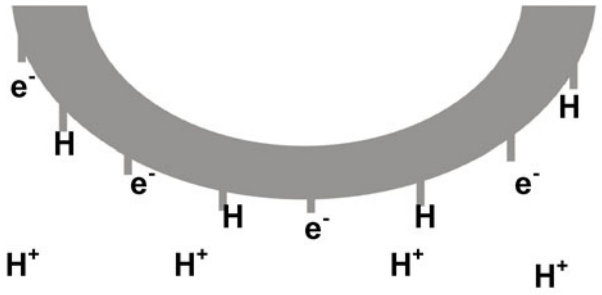

Fig. Potential formation

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The silicate of the membrane is electrically negatively charged. Hydrogen ions carry a positive electric charge. The bound hydrogen ions and the silicate mutually balance out their electric potentials. During the measurement, the membrane exchanges hydrogen ions with the measured media until a balance is established between the two media. The number of hydrogen ions bound to the membrane depends on the activity of the hydrogen ions in the measured solution. With a low pH value, the activity of the hydrogen ions is very high, and many hydrogen ions means many bound ions on the membrane. The negative potential of the silicate is very largely balanced out. With a high pH value, the activity of the hydrogen ions is very low. Few hydrogen ions means few bound ions on the membrane. The membrane is highly negatively charged.

High impedance

Glass is a bad electrical conductor, i.e. the resistance is very high. The electric charge on the membrane is very small. The implication of this for the measurement is that the pH meter and all electrical connections must have a very high resistance $R \geq 10^{12}\ \Omega$. Any leakage current (e.g. from moisture or the wrong type of cable) causes measurement errors and can damage the electrode. The distance between the electrode and the transmitter should be as short as possible. In the simplest case, a basic 2-wire transmitter near the measurement point will suffice.

Information on pH measurement

Membrane shapes

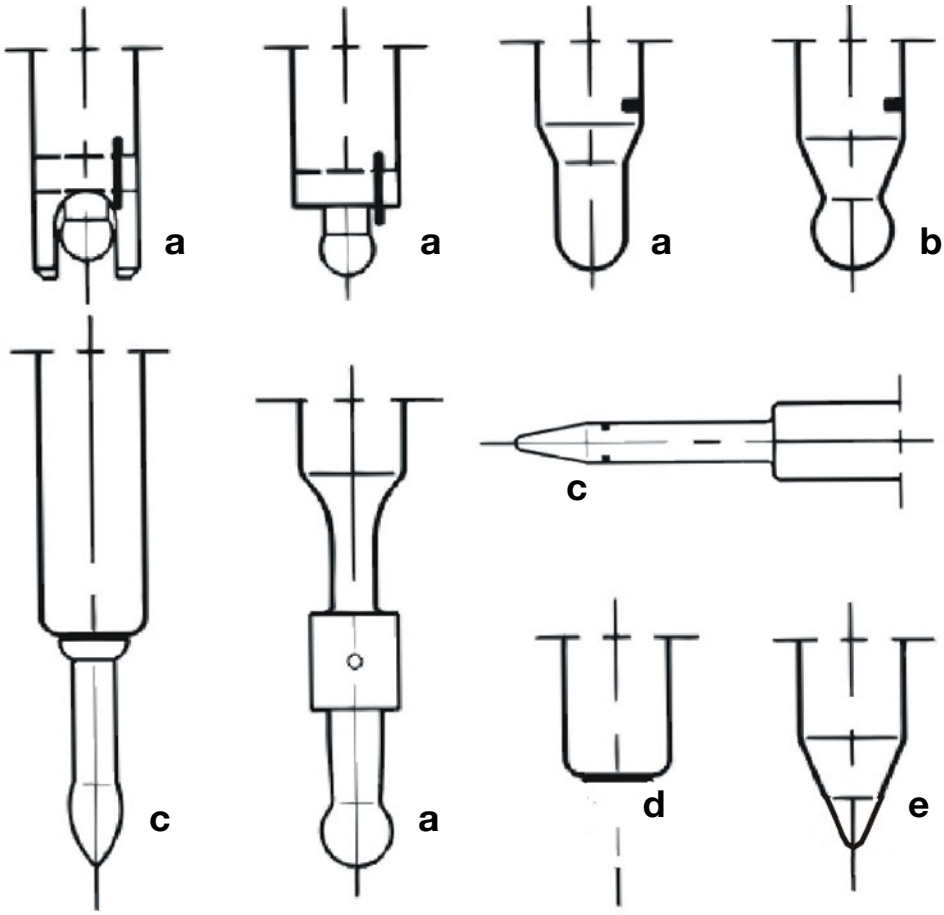

Fig. Membrane shapes

The optimal shape of the membrane is arranged to suit the application. A cylindrical shape (a) or spherical shape (b) are suitable for aqueous solutions. These membranes are robust and easy to clean. For insertion measurements, e.g. in fruit and meat, pointed needle membranes (c) are more suitable. For measurements on surfaces, a flat membrane (d) ensures good contact with the surface, e.g. skin or paper. The cone membrane (e) is an optimal shape for many process applications. It is robust and has a good self-cleaning action in flowing measured solutions.

Reference electrode

The reference electrode complements the pH electrode to form an electrode system. Its construction and condition has a considerable influence on the reliability of the measurement and the required maintenance costs.

The most widely used type is the silver/silver chloride electrode (Ag/AgCl). This reference electrode has proved itself and gained acceptance for most applications. Other types of reference electrodes such as calomel, copper/copper iodide and thalamide, are not used now, or are no longer used as often.

The most important components of the reference electrode are: a conductive wire, an electrolyte and a connection between the electrolyte and the measured solution.

How does a silver/silver chloride reference electrode work?

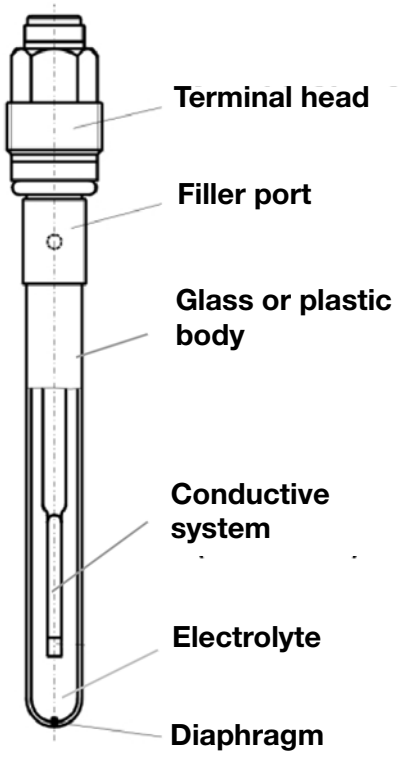

Fig. Reference electrode

In the simplest case, the conductive system is a silver wire coated with silver chloride. It has two functions, firstly to connect the electrolyte to the connecting cable, and secondly to provide the stable electrical reference point for the voltage measurement. The conductive wire operates like an ion-selective chloride electrode. Its potential depends on the chloride concentration of the reference electrolyte. A concentrated potassium chloride solution ($c_{(KCl)}$ = 3 mol/l) is used as the electrolyte. As the chloride concentration of the electrolyte remains virtually constant, the potential of the reference electrode is stable too.

Instead of the coated silver wire, some electrodes contain a cartridge filled with silver chloride. Inside the cartridge, the electrolyte becomes saturated with the silver chloride. The remaining electrolyte within the reference electrode stays virtually free of silver ions. With reference electrodes using this type of cartridge, there is no problem due to silver compounds that are difficult to dissolve, such as the familiar “black diaphragm” caused by silver sulfide. At low conductivity, the system does away with the special potassium chloride solution ($c_{(KCl)}$ = 1 mol/l), once common for such applications.

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The electrical connection can be established by, for example, a diaphragm that is permeable to the electrolyte. Electrolyte ions move through the diaphragm into the measured solution and transport electric charges in this way. The more permeable a diaphragm, the more reliably the charge transport functions, and the more stable is the potential of the reference electrode. However, the increased electrolyte consumption also reduces the service life of the electrolyte.

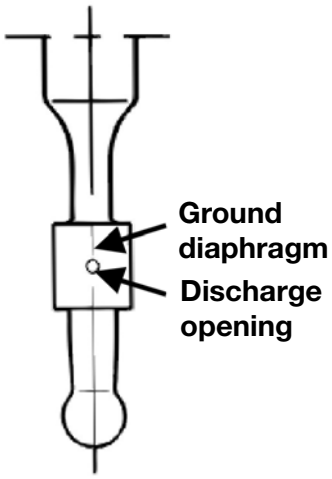

Fig. Ground diaphragm

As with the membrane, the optimal diaphragm also depends on the particular application. Ceramic diaphragms consist of a porous ceramic pin. The electrolyte only flows slowly through the pores into the measured solution. This type of electrodes has a long service life. The ceramic diaphragm is especially suitable for water treatment for swimming pool water and drinking water. Here, electrodes with multiple diaphragms reduce the sensitivity of the measurement system to flow.

For heavily polluted water, such as waste water, a teflon ring is more suitable. Fine-pored ceramic pins contaminate too quickly in this water. With a teflon ring, the large contact surface prevents rapid contamination.

In the same way, a ground diaphragm has a large contact surface. This diaphragm is only used with electrolyte solutions. Electrodes of this type have proved very successful for water with a low ion content (low conductivity).

Depending on the application, the reference electrode is filled with an electrolyte solution, electrolyte gel or polymerizate. The transition points here are relatively flexible. The traditional electrolyte is a potassium chloride solution $c_{(KCl)}$ = 3 mol/l. In the laboratory, electrodes with an electrolyte solution normally give the best results. This type of electrolyte establishes the most reliable contact with the measured solution.

For continuous measurement in clean water, such as drinking water, swimming pool water or ground water, the service life of a potassium chloride solution is too short. Even with a ceramic diaphragm, the loss of electrolyte results in unacceptably short maintenance intervals of only a few weeks. In such cases, thickening the electrolyte slightly and providing it with a salt reservoir has proved successful. The reference electrode is filled almost “brim-full” with potassium chloride. This salt reserve can still be seen in crystalline form inside the reference electrode even after the measurement system has been commissioned. This reserve is one of the main reasons for the exceptionally stable measuring behavior and service life of these electrodes.

The electrolyte gel is a high-viscosity or soft paste form of electrolyte. One of its outstanding properties is its pressure resistance, which is why these electrodes are the only practical solution for measurements in pressurized pipelines and vessels. The high viscosity also permits the use of a large surface contact with the measured solution, via the annulus of a teflon ring, for instance. The teflon ring in combination with an electrolyte gel is the ideal design, for example, for measurements in waste water or contaminated surface waters.

3 Measurement

Until now, the basis of pH measurement has been the glass electrode. It is the method of the national and international standards and reference procedures. All other methods are employed to cover applications where the measurement either cannot be made with a glass electrode or has other drawbacks (e.g. short service life or high maintenance cost).

Depending on the application, pH measurements can be made in the laboratory, on site with a hand-held pH meter, or continuously in a process.

Online measurement is essential for all applications where a full picture of the pH behavior of the water is required; this applies particularly to control systems, of course.

A hand-held pH meter can be a valuable aid for checking the process measurement setup. With the correct documentation, the comparison measurements provide information on the status of the process measurement setup at any time. Calibration and maintenance timings can be determined precisely by comparison measurements.

3.1 Arrangement of a process measurement setup

The term measurement setup includes the full set of instruments and equipment used for pH measurement, consisting of:

- pH sensor: pH and reference electrodes or combination pH electrode
- immersion or flow-through fitting
- screened instrument cable
- transmitter/controller (mV meter)

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3.1.1 Electrode

Fig. Combination electrode

The combination pH electrode consists of a pH glass electrode surrounded by the reference electrode. The shaft can be made of glass or plastic. The important structural elements of this application are the filling material of the reference electrode, the electrolyte, and in addition, an opening at the bottom end of the reference electrode, the diaphragm, and a rounded glass tip at the bottom end of the electrode – the glass membrane.

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Electrolyte and diaphragm

The electrolyte and the diaphragm must be matched to one another according to the application. For heavily contaminated liquids, such as waste water, suspensions or emulsions, diaphragms that are insensitive to contamination are required, e.g. annular or ground. A stiffened electrolyte, gel or polymerizate, reduces the electrolyte outflow and with it the maintenance costs.

For water that is optically relatively clear, such as swimming pool water and drinking water, electrolyte solutions (possibly thickened slightly) are more suitable. Because of the lower viscosity, fine-pored diaphragms, such as ceramic or glass fiber diaphragms, are necessary in this case.

For many applications, the electrolyte must contain no silver ions, or as few as possible. Solutions containing sulfide, and even water with a low salt content, form silver compounds in the diaphragm that are difficult to dissolve, and this can lead to degradation of the pH measurement.

Membrane shapes

The membrane can be manufactured in different shapes, depending on the application. The spherical and rounded tip membranes are particularly robust for operational use. These electrodes have a low susceptibility to wear and are easy to clean.

Integrated temperature sensor

The temperature is a fundamental item of information for the temperature compensation function of the transmitter, and it often has to be documented as additional information for the pH value as well. Because of this, electrodes that already incorporate a temperature sensor are particularly beneficial. Only one connecting cable and installation point is required for both sensors. However, there were problems until now, as each manufacturer developed his own connection system, which meant that measurement devices from different manufacturers were not compatible. Because of the fully justified demands made by users, a team of experts at NAMUR[1] tested the various connection systems against defined criteria.

SMEK terminal head

Fig. SMEK terminal head

The result was a clear recommendation for the SMEK connection favored by JUMO. However, measurement systems with the very robust VP (Variopol/Variopin) terminal heads are available on request. Because pH electrodes involve parts subject to wear, careful consideration should be given as to whether versions with integral temperature probes should be used: each time the electrode is changed, the temperature probe is scrapped as well, and a replacement has to be paid for along with the new pH electrode.

1. NAMUR: Standards organization for measurement and control technology in the chemical industry.

3.1.2 Fittings

Fittings are used for holding and protecting the sensors (glass electrode, reference electrode, combination pH electrode). Immersion fittings permit measurements not only at the surface of the liquid, but also deep inside it. A wide range of mounting elements and accessories permit mounting on almost all vessels. The immersion fittings are normally manufactured from polypropylene (PP), and are supplied in immersion lengths up to 2000 mm. However, other materials (e.g. V4A) are also available for special purposes. Flow-through fittings permit measurement directly in the liquid flow lines or in the bypass of these lines. As well as the electrode, the fitting can also contain a temperature sensor and/or an impedance converter (see Chapter 3.1.3)

It is essential that all fittings are mounted in an easily accessible position, to permit regular servicing and maintenance of the sensors. It should be possible to change the sensor at any time without undue effort.

3.1.3 Shielded instrument cable

Fig. Shielded instrument cable

In order to ensure optimum transmission of the measurement signal, only special low-loss coaxial cables are used in pH measurement. They establish the electrical connection between the sensor and the transmitter.

The pH cables have a special construction. In addition to the copper screen, there is also a semiconducting layer. Commercial grade antenna or computer cables are not suitable.

Because of the high-impedance nature of the pH electrode, the cable must not be run via terminals. In addition, the cable length should be kept as short as possible - if only for the sake of the measurement system calibration. With cable lengths above 15m for example, the use of an impedance converter (JUMO Data Sheet 20.2995), that screws on to the electrode, is recommended. It reduces the high internal impedance of the electrode and allows good signal-stabilized transmission of the measured value to the connected transmitter.

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3.1.4 Transmitter/controller

One of the tasks of the transmitter is to convert the high-impedance signal of the pH electrode to the pH scale, and to make this available once again as an indicator and/or standard signal. The transmitter normally incorporates a calibration routine for adjusting the electrode with buffer solutions.

The transmitters are often designed to operate as controllers at the same time, so that they can perform dosing of acids and alkalis for pH correction, for example. In addition, the transmitter takes account of the temperature, either

by a manual entry option, or by a separate measurement input for the temperature sensor.

Fig. Modern pH transmitter / controller JUMO dTRANS pH 01

3.2 Commissioning the measurement setup

3.2.1 Measurement location

The choice of an optimal measurement setup is followed by the commissioning. This includes not only the installation of the measurement setup, but also the choice of the correct measurement location. The measurement setup only indicates the pH value prevailing at the location of the measurement at the time. Recommendations for selection of the measurement location are given in application-oriented standards and regulations. In Germany, these include DIN 19643 for measurement of swimming pool water and specification M 256 issued by the Association of Waste Water Authorities (ATV).

3.2.2 Measurement conditions

The optimum measurement requires a knowledge of several important variables that influence the pH measurement.

Temperature

The electrode voltage depends on its temperature. Whereas the output of the measurement system for a pH value pH = 8 is around -56 mV at 10°C, the output for the same pH value at 25°C is now -59 mV. The transmitter must know the temperature of the electrode to be able to calculate the correct pH value. At relatively constant temperatures, it is sufficient to adjust the temperature value at the transmitter manually (e.g. in swimming pools). With fluctuating temperature conditions, a transmitter with a temperature sensor is recommended. The instrument automatically adjusts the value of the electrode slope for the current temperature.

Information on pH measurement

The following table gives an idea of the pH deviation relative to the temperature difference between the set value and the actual value of the measured solution.

Deviation from the set temperature	pH value										
	2	3	4	5	6	7	8	9	10	11	12
-20	0.34	0.27	0.20	0.14	0.07	0.00	-0.07	0.14	0.20	0.27	0.34
-15	0.25	0.20	0.15	0.10	0.05	0.00	-0.05	0.10	0.15	0.20	0.25
-10	0.17	0.14	0.10	0.07	0.03	0.00	-0.03	0.07	0.10	0.14	0.17
-5	0.08	0.07	0.05	0.03	0.02	0.00	-0.02	0.03	0.05	0.07	0.08
-1	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.02
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.02
5	0.08	0.07	0.05	0.03	0.02	0.00	-0.02	0.03	0.05	0.07	0.08
10	0.17	0.14	0.10	0.07	0.03	0.00	-0.03	0.07	0.10	0.14	0.17
15	0.25	0.20	0.15	0.10	0.05	0.00	-0.05	0.10	0.15	0.20	0.25
20	0.34	0.27	0.20	0.14	0.07	0.00	-0.07	0.14	0.20	0.27	0.34

Pressure

Pressure has an effect, firstly on the reference system of the reference electrode, and secondly on the pH value. The effect on the reference system can easily be taken into account by choosing a suitably pressure-resistant electrode. Interpretation difficulties with comparison measurements occur in certain cases. In waters that contain pH-active gases like ammonia, carbon dioxide or hydrogen sulfide, the pressure changes the pH value. In basic solutions, the pH value increases with rising pressure, and in acidic solutions it reduces. If a comparison measurement is made under normal pressure conditions, the measurement result is correspondingly higher or lower. At lower pressures, the effect is often increased as the dissolved gases effervesce.

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Flow

Continuous measurements almost always take place in flowing water. Each electrode reacts more or less strongly to the water movement. Although brand new electrodes are relatively insensitive to changes in flow, the effect can cause considerable deviations in measured values with spent electrodes.

Regular checks on the sensitivity to flow provide information on the status of the electrode. If the sensitivity to flow is too high, the electrode should be replaced.

3.2.3 Installation

Installing the individual components in a systematic manner gives an initial indication of the correct operation of the electrode.

First of all the transmitter is installed. Testing with a voltage source (pH simulator) demonstrates that it is working correctly.

The next step is to connect the pH sensor (sensor with fitting). A comparison measurement between the water in a bucket (or some other ungrounded container) and the intended measurement point can give an indication that the sensor is in good condition. The two values must agree, taking into account the variations with time (decomposition process). The diaphragm and the membrane must be fully immersed in the water for both measurements.

If this test indicates that there is no fault, connection of the peripheral equipment (recorder, dosing device, controller, etc.) can start. After each item of equipment is connected, a check should be made on whether the value indicated by the transmitter has changed significantly.

3.2.4 Calibration

After installation, the transmitter must be adjusted to the electrode. Three methods are available for this, the single-point, two-point and three-point calibration methods.

Single-point calibration

The single-point calibration is the optimal method for applications where the comparison measurement can only be made with a hand-held instrument.

For this method, the pH value is measured as close as possible to the measurement point of the transmitter, using a calibrated hand-held meter. The indicated value of the transmitter is then simply set to the value of the hand-held meter by adjusting the system zero point.

Two-point calibration

The two-point calibration is the most common method for pH measurement.

Two buffer solutions are used for the calibration, e.g. with pH values pH = 7 and pH = 4. Because of their instability, there is nothing to be gained by using basic solutions. Although microprocessor instruments permit any sequence of buffer solutions, it makes sense to start with a neutral solution pH = 7.

Three-point calibration

If the calibration has to cover a particularly wide range, a third point extends the calibrated range. This can be worthwhile, for example, if the range has to extend from pH = 4 to pH = 9.

3.2.5 Buffer solutions

pH buffer solutions are used as a means of calibrating pH electrodes. They are aqueous solutions with known pH values. Buffer solutions are categorized into primary reference buffer solutions, secondary reference buffer solutions and technical buffer solutions, according to their properties.

Primary reference buffer solutions show the lowest uncertainty in pH values (U(pH) = 0.003). They are used mainly in metrological institutes and are not

available commercially.

Secondary reference buffer solutions have the same composition as primary solutions. The uncertainty of the pH values is around U(pH) = 0.006. These solutions are needed by manufacturers of technical and working reference buffer solutions, and by control and quality assurance laboratories.

Technical buffer solutions are solutions for practical use; their uncertainty is in the range from U(pH) = 0.01 to U(pH) = 0.05. Technical buffer solutions are the robust solutions. They are relatively immune to contamination and dilutions, and so are best suited for calibration of plant and hand-held meters.

There are pH buffer solutions for almost the entire range of the pH scale. For routine work, two solutions with pH values of approx. pH = 7 and pH = 4 are adequate for a pH range from pH = 2 to pH = 10. Basic buffer solutions are often very unstable and many pH electrodes react very sluggishly in them. Because of this, the slopes in basic solutions are shallow in most cases. Practical calibrations with basic buffer solutions can only be achieved by excluding air from the solutions and allowing a relatively long settling time. This effort is only worthwhile for measurements in the laboratory.

People often talk about the traceability of the buffer solutions. The traceability concerns the pH value of the pH buffer solution. It means that the pH value was tested by the manufacturer either directly against a primary reference buffer solution, or via intermediate solutions (e.g. secondary reference buffer solution).

Example

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tech. buffer solution	→	sec. reference buffer solution	→	prim. reference buffer solution
or		tech. buffer solution	→	prim. reference buffer solution

The traceability of the pH value forms a basis for calculating the uncertainty.

4 Quality assurance

Formerly, the idea of quality assurance related mainly to the manufacture of products such as hi-fi equipment, measuring instruments or cheese. Analysis was just a means of proving the quality. Within the framework of Good Laboratory Practice (GLP) and certification procedures, e.g. in accordance with ISO 9000, laboratories also have to concern themselves much more with questions about the quality of measurement and measured values, in the context of standard operating procedures (SOPs). This is a constantly ongoing process, so that nowadays regulations concerning quality assurance must be complied with in process measurement as well. Examples of this in Germany include the specifications issued by the Regional Water Authorities (LAWA), the Directive ENV ISO 13530 embodied in the unified methods for testing water and waste water, or the ATV specification ATV-DVWK M 704.

4.1 How accurate is the pH measurement?

It is almost impossible to answer a question on the accuracy of measurements. A statement of the accuracy presupposes that the true value is known, which is not the case in practice. The uncertainty of a measurement can be estimated. However, the term “estimate” should not be associated with the term “approximate”, but rather with an informed assessment.

The statement that the uncertainty U(pH) is ± 0.4 means that there is a 95% probability that the true pH value of the measured solution will not deviate by more than ΔpH = 0.4 from the measured value. If the value for the uncertainty is halved, the probability is now only 67%.

A knowledge of the uncertainty can be of special significance for operational measurement. The important thing here is, for example, when a limit is exceeded.

Example

A limit value of pH = 7.6 is specified for the pH value and the measured value is pH = 7.4 with an uncertainty of U(pH) ± 0.4. Although the measured value pH = 7.4 is still below the limit, there is still a risk that the limit is being infringed. So there is a very good possibility that a comparison measurement would give a value of pH = 7.7. Only when the measured pH value is less than 7.2 can an infringement of the limit be almost (but not completely) ruled out.

Quality assurance measures make a fundamental contribution towards reducing the uncertainty.

4.2 Documentation

A fundamental component of quality assurance is the documentation of all information relevant to the measurement. The records serve as proof of the condition of the measurement setup and, of course, the measured product. Measurements collected over a longer period of time are a good basis upon which to make decisions, for example:

- ❏ on maintenance of the measurement setup
- ❏ on control of the water parameters

- ❏ on troubleshooting in the event of a fault
- ❏ or for the acquisition of new measurement equipment.

An essential requirement for these and other options is the complete documentation of the measured values and the conditions under which the values were obtained. This includes the measurement conditions, dates of the calibrations and tests, together with information on the measurement setup used.

The documentation must be complete and arranged so as to be easy to read and understand, so that the facts of a matter can be clarified even after long periods of time.

The measured values are normally already recorded by the transmitter. For dosing and control systems, it is recommended that additional records of measurements made with hand-held meters are maintained. A control system indicates the setpoint independently of its status. The controller compensates for a drift in the electrode by an increased acid or base dosing, for example. Comparison values indicate this incorrect dosing and the extent of the deviation.

General information

A log should contain all data about the measurement point, the measurement setup and any service work that may have been carried out:

- ❏ designation and location of the measurement point
- ❏ full address of a contact person
- ❏ serial numbers of the components of the measurement setup
- ❏ purchase date and commissioning date of the measurement setup
- ❏ date and reason for repair works
- ❏ name and address of the service provider for service and repair work.

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Calibration data

A calibration record should include the following data:

- ❏ designation and location of the measurement point
- ❏ serial numbers of the components of the measurement setup
- ❏ name of the responsible person
- ❏ designation, serial number and use-by date of the buffer solution used
- ❏ type of calibration (single-point or two-point method)
- ❏ date and data of the calibration (e.g. flow behavior, response behavior, system zero, slope).

Measured values

In addition, records of measured values should also include the date and time and any relevant accompanying parameters, e.g. statement of the temperature.

Other information

To complete the documentation, descriptions of the measurement methods used, including the descriptions of the calibrations, adjustment procedures and the maintenance and storage of the measurement setup must be included. In addition, all operating instructions and other specifications and

instructions must be filed in the documentation folder.

4.3 Maintenance

The ageing of a measurement setup, and particularly electrodes, is dependent on the measurement conditions. Wear and contaminants restrict its reliability and cause deviations. Regular calibration helps to detect unreliable components and to restore them to optimum condition by cleaning, for example.

A fault in the measurement function that occurs in the interval between calibrations can only be detected by means of the recorded values.

A fault can show itself through scattered measured values or by measured values that deviate from previously accustomed empirical values. The decision on whether this is a normal event or whether an intervention is required must be made on the basis of the documented data.

Scattered measured values

Scattered measured values alone are not always an indication of a fault. The scattering can be caused by normal variations in the water, or in the measurement procedure.

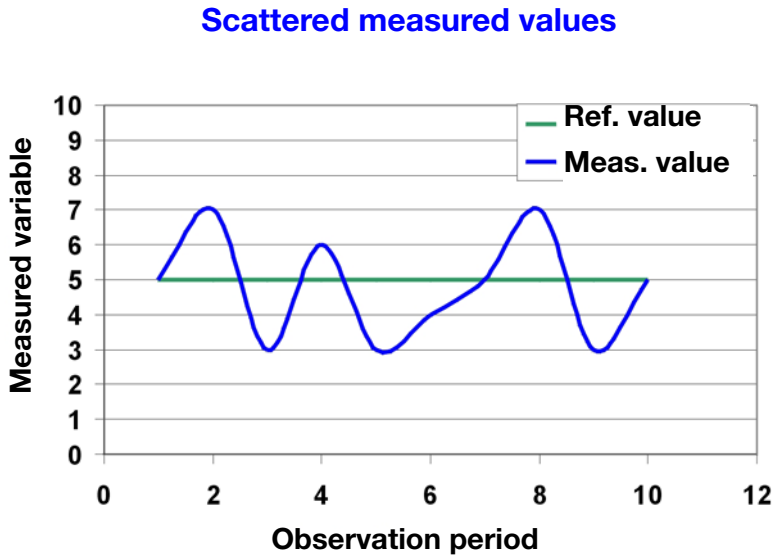

Fig. Scattered measured values

The scattering of the measured values increases more and more with the age of the electrode. This effect is particularly marked with hand-held meters. The cause can be a usage-related sluggishness of the electrode. With continuous measurements, this effect is made noticeable by scattered calibration data and mainly by small slope values.

The cause of the sluggishness can be a spent electrolyte or a membrane contaminated with lime, for example.

A sluggish electrode only costs operating time, but can also cause problems with dosing and control systems.

The measure of the scattering is the standard deviation, e.g. s = 0.07. This value states that two out of three values deviate by a maximum of ΔpH = 0.07

from the mean value of the measurement results. Every third value deviates by more than ΔpH = 0.07 from the mean value. In Germany, the Regional Water Authorities (LAWA) recommend a deviation value of double the value of the standard deviation as a warning limit; in our example, this corresponds to a deviation of ΔpH = 0.14. This deviation is so high that it can hardly be accidental. Maintenance of the electrode is strongly recommended.

If a measured value deviates from the mean value by more than three times the standard deviation, the situation is out of control, that is an appreciable change in the measurement conditions or the electrode. It is strongly recommended that the cause should be clarified, even if the measured value is still within the permissible range for the process.

Drifting measured values

The phenomenon referred to as “drift” is a normal characteristic of an electrode. The measurement setup (or, in the case of a control system, the handheld meter) indicates permanently increasing or decreasing pH values.

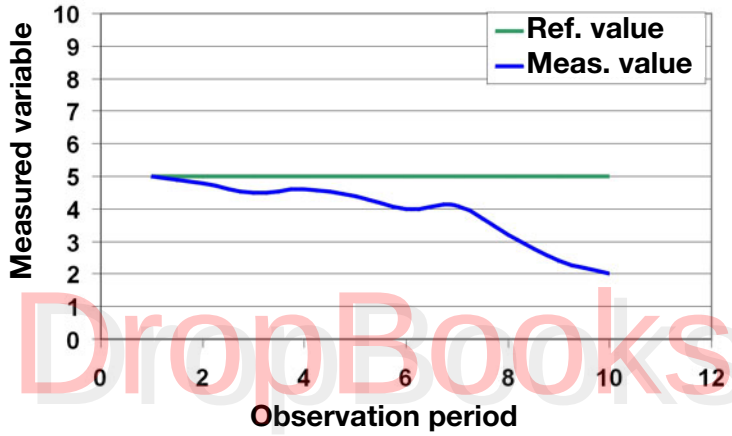

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Fig. Drifting measured values

The cause of the drift is normally the reference electrode. Loss of electrolyte, increasing sensitivity to flow, and also contaminations, change the potential of the electrode. This change in potential shows itself in the drift of the measurement setup. The drift caused by the electrolyte loss accelerates at the end of the service life to such an extent that it can only be remedied by changing the electrolyte solution or the electrode.

Contaminations occur when, for example, sulfide ions from the water penetrate into the reference electrode and convert the silver/silver chloride system to a silver/silver sulfide system. Cyanide ions can damage the silver/silver chloride system, as they dissolve the silver chloride.

Electrolyte consumption and contamination cause a pronounced shift in the system zero during calibration. A sensitivity to flow is often not noticeable during calibration. The effect can be seen more clearly by moving the electrode gently in the water. The value indicated by the setup when the electrode is being moved is different from the value when the electrode is kept stationary.

Sudden deviations

If a significant change in value occurs within a few minutes, the likely cause is an electrical fault. However, it could simply be that the electrode is no longer fully immersed in the water.

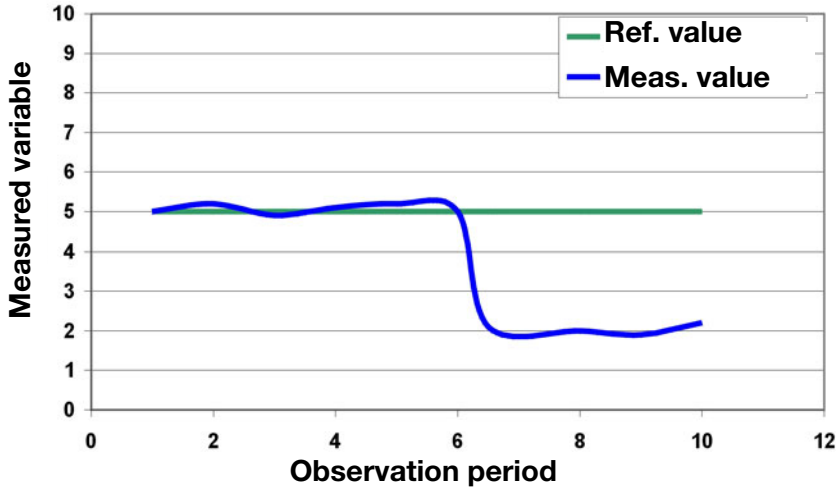


Fig. Sudden deviation

An electrical fault causes a constant deviation. In many cases, the deviation also occurs periodically when a source of interference voltage is switched on and off.

Extremely unstable values

If the transmitter indicates unrealistic and very unstable values, this indicates a break in the circuit, e.g. a break in the cable, broken electrode, or an open-circuit contact in a socket. The electrode can also produce very unstable values when the diaphragm is blocked by lime, grease, or oil, for example.

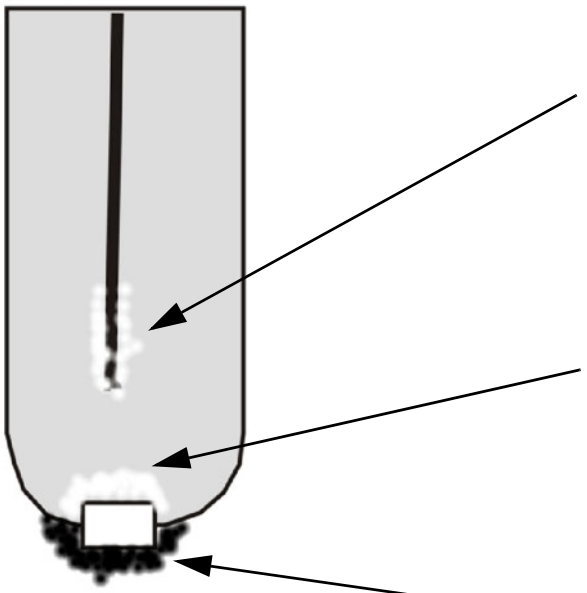
No reaction

If the indicated value stays the same even after the measured solution is changed, this is a clear indication of a short circuit or a shunt circuit. The instrument usually indicates values in the range pH = 7 ± 0.5.

Moisture

If moisture penetrates the electrical connections, the electrode behaves in a similar way to a spent electrode. In contrast to a spent electrode though, the symptoms occur more clearly and in a considerably shorter time. The electrode will often show correct values again, once the moisture has evaporated.

4.3.1 Critical effects on the reference electrode



Reduction
- grounding
- damp connector and cable
- incorrect wiring
- semiconducting layer not removed

Contamination
- sulfide
- cyanide
- ammonia
- heavy metals
- reducing agents

Blockage
- coatings
- grease
- albumen
- organic substances
- surfaces drying out

Fig. Reference electrode

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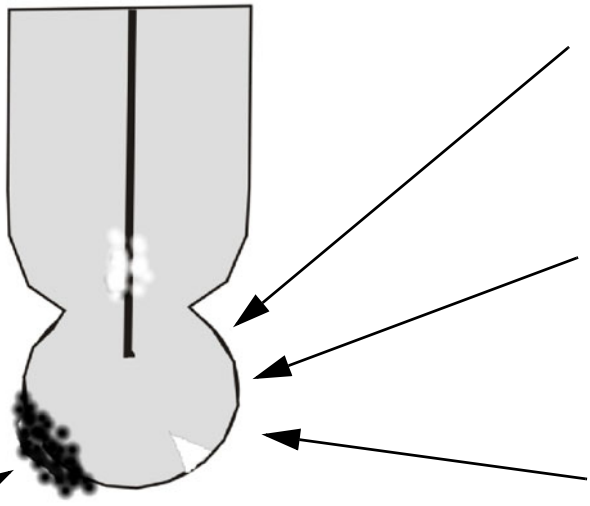
4.3.2 Critical effects on the pH electrode



Ageing
- high temperature
- extremely high or low pH values

Chemical
- hydrofluoric acid pH < 5
- strong alkali, NaOH
- strong acids, hydrochloric acid

Mechanical
- hairline cracks
- sand
- stones
- shocks/vibrations

Coatings
- lime
- gypsum
- grease
- albumen

Fig. pH electrode

4.4 Cleaning

If the behavior of the measurement setup indicates an electrode malfunction, the most effective way to clear the fault is by cleaning. The cleaning agent used basically depends on the type of contamination. In most cases, warm water with some household washing-up liquid is sufficient to remove grease and oil. Lime or iron oxide deposits can be removed with vinegar, citric acid or dilute hydrochloric acid.

Never mechanically clean the membrane. Even wiping or drying the membrane can lead to faults in the measurement function.

After cleaning, rinse the electrode with deionized (distilled) water.

4.5 Calibration

It is recommended that calibration is carried out after each maintenance operation (e.g. cleaning or changing the electrode), at the latest after about 3 to 4 weeks operating time.

4.6 Storage of the electrode

Electrodes have only a limited shelf-life. Stocks on hand should be used up within about a year.

Do not leave an electrode connected to a switched-off instrument for a long period. Thoroughly clean the used electrode and store it.

To store the electrode

- ❏ close off the filler opening if there is one
- ❏ fill the protection cap with electrolyte solution
- ❏ insert the cleaned electrode into the protection cap
- ❏ during longer storage times, check regularly that there is sufficient electrolyte in the protection cap.

Store the electrode in such a way that no moisture can enter the connector.

5 Applications

pH measurements are found in all areas of technology and environmental protection. Depending on the application, the measurement takes place in the laboratory, on-site with a hand-held meter, or continuously, in a process environment, for example.

The following practical applications should be considered in more detail. Measurement of the pH value in:

- ❏ waste-water treatment plants
- ❏ swimming pools
- ❏ electroplating plants
- ❏ power stations
- ❏ water supply systems
- ❏ reservoirs

5.1 Waste-water treatment plants

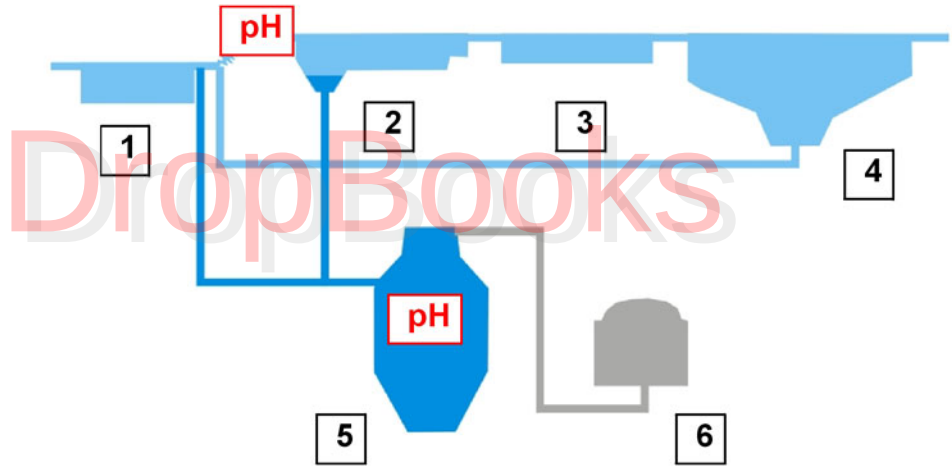


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Fig. Diagram of an urban waste-water treatment plant

1 Sand trap	4 Post-clarification basin
2 Preclarification basin	5 Biotower
3 Activated sludge basin	6 Gasholder

Some pH measurement setups used in waste-water treatment plants are subjected to extreme stresses:

- ❏ The water is highly contaminating. In some cases the substances contained or the physical conditions subject the sensors that are used to stress.
- ❏ A corrosive atmosphere affects the electronic part of the measurement setup.
- ❏ Maintenance work must be possible even under tough conditions.

In Germany the ATV specifications are available for analysis in water. pH measurement is described in specification M 256.

5.1.1 Inlet to the plant

The pH measurement in the inlet to the plant serves to protect the sewer system and the structures. Waste water with a pH value below 6 or above 9 results in costly material damage. Normally, exceeding or falling below the permissible pH range for a short time is of no consequence. The larger quantities of water in the basins of the plant are sufficient to adequately dilute and neutralize smaller quantities of acids or bases. However, when there are long-term or frequent infringements, the cause must be found and the inflows eliminated. If the monitoring of the inlet is to be effective, it must operate continuously, round the clock. A permanently installed measurement system with suitable recording means is required for the measurement.

Measurement setup

The large quantities of fibrous contaminants as well as grease and oil pose a problem for the pH measurement by becoming entangled or forming a coating on the pH electrode. Electrodes that have been contaminated in this way become extremely sluggish and produce false measured values.

The fitting must have as smooth a shaft as possible, and be freely suspended at a position with the best possible water flow. Any tangled fibers on the fitting must be removed at regular intervals.

To avoid the reference electrode clogging rapidly, it should have an annular diaphragm. Basically, it is advisable to clean the electrode every 14 days, depending on the loading. Grease and oil deposits can be easily removed with a little washing-up liquid and warm water.

In waste-water treatment plants, lightning strikes are one of the most common causes of severe damage to the measurement setup. For this reason, the transmitter must have a good surge voltage protection.

5.1.2 Biotower

General

An additional measurement point for the pH value is the sludge in the biotower. The pH value has a significant effect on the activity of the micro-organisms. The micro-organisms occurring in this anaerobic process react much more sensitively to their environmental conditions than aerobic forms. Even with only small pH variations, some populations disappear and others are formed.

With a pH value below 7 (neutral point) the sludge breaks down (acid sludge) and evil-smelling decomposition gases are formed (including hydrogen sulfide). The desired reduction in volume proceeds even more slowly and only to a limited extent. The sludge so formed is slimy and is difficult to dehydrate.

Under basic (alkaline) conditions, in the range from pH = 7 to pH = 8, the desired odorless methane decomposition occurs. Precise monitoring and adjustment of the pH value is an essential requirement here for optimal methane gas production.

Information on pH measurement

Measurement setup

Permanent pH monitoring can realistically only be achieved with a sensor mounted direct in the main pipeline, i.e. a fixed measurement setup. The sensor is exposed to increased stress with these measurements:

- ❏ A high solids content in the sludge leads to heavy contamination.
- ❏ Excess pressure stresses the reference system of the pH measurement system.
- ❏ Hydrogen sulfide poisons the reference system.

Check measurements

Checks on the fixed measurement setup must be made directly in the waste water, that is in the sewer or basin. Biological degradation processes, or redox reactions, for example, can easily call the result of a measurement in the laboratory into question, no matter how precise it is. An on-site measurement with a hand-held meter is better.

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5.2 Swimming pools

In Germany, monitoring of the pool water is specified in §11 of the Federal Epidemic Law and the swimming pool regulations of the various states. DIN 19643 contains more detailed information on the pH value and chlorine content. The pH value and the chlorine content are the most important parameters here. The pH value must be within a range from 6.5 to 7.5.

With a pH value above 7, bases absorb a portion of the acid disinfectant. The higher the pH value, the less is the effect of the disinfectant.

Example

At pH = 8, the concentration of the hypochlorous acid is reduced to 30%. In addition, high pH values reduce the effect of the flocculation agents and encourage the formation of deposits on the walls of the pool. At pH values of 8 and above, the bases eventually destroy the natural protection of the skin.

At too low pH values, acids attack the pool material, and, for their part too, reduce the effect of the flocculation agent and increase the formation of combined chlorine (chloramines).

pH value	Effect
	Skin irritation
8.5	
	Lime turbidities
8.0	
	Impaired Al-flocculation
7.5	
7.0	**Indoor swimming pool odor**
6.5	
	Corrosion phenomena
6.0	
	Impaired flocculation

Information on pH measurement

Measurement

A pH control unit in the water treatment plant adjusts the pH value to the optimal value of about pH = 7.2. This pH value ensures economic operation of the plant. The adjustment is made by controlled addition of acid or base. The measurement point is normally between fiber trap and filter. However, a measurement can also be made directly in the pool itself.

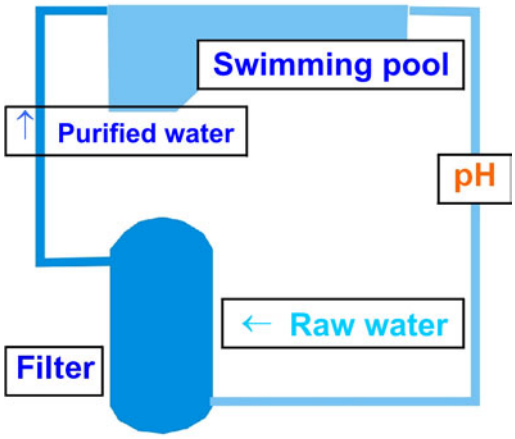

Fig. pH measurement in a swimming pool

The pH electrode is hardly exposed to any contaminants in the pool water. Electrodes systems with electrolyte solution (possibly slightly thickened) and ceramic diaphragms have the best measurement behavior here. The style used must be designed for an excess pressure, even if this is only slight, in the measured pipeline. Electrodes with a reference electrolyte gel age very rapidly. As well as the more frequent outlay for new electrodes, this also results in increased maintenance costs and poorer control results.

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5.3 Electroplating plants

The pH measurement is used for monitoring of electroplating baths and decontamination processes.

5.3.1 Electroplating baths

In an electroplating bath, a protective coating is applied to objects made of base metals, such as zinc or iron. This can be a copper or nickel coating, for example. A zinc coating can work as corrosion protection with iron, as the zinc plating of automobile bodies shows.

The metal coating is normally applied electrolytically in special baths. Some examples of this type of process are:

Acid copper bath:
A combined solution of sulfuric acid and copper sulfate.

Cyanide copper bath:
A solution of copper cyanide, sodium cyanide and sodium carbonate.

Diphosphate-copper bath:
A nearly neutral solution of potassium dihydrophosphate,
copper diphosphate, ammonia, and luster additives.

Nickel bath:
A solution of nickel sulfate, nickel chloride, and boric acid with a pH in the range from pH = 3.5 to pH = 4.5.

Acid zinc bath:
Zinc sulfate, zinc chloride, sodium sulfate and sulfuric acid with a pH in the range from pH = 3 to pH = 4.

Alkaline zinc bath:
A solution of zinc cyanide, sodium cyanide and sodium hydroxide.

Measurement

Electroplating baths impose special demands on the pH measurement, particularly with continuous measurement.

Electrochemical pH measurement is based on measurement of voltage in the range from a hundredth to a few tenths of a volt. The current flowing here is negligibly small. For a galvanic coating, if more than 1V is applied to the bath, currents of up to 10 A per dm^2 will flow, and if the measurement setup is earthed then current will flow through the reference electrode. In this case, the measured value indication depends on the voltage of the electroplating process.

A further problem is the temperature, that can reach 80°C. As a rule of thumb, it can be taken that a temperature increase of 10°C halves the service life of the electrode. Special high-temperature electrodes are required, particularly in the upper temperature range.

5.3.2 Decontamination

Cyanide decontamination

The removal of cyanides from waste water is another example of the industrial application of a pH measurement. Waste water containing cyanides is treated in continuous-flow treatment plants. These plants consist of the following components:

- reactor (vessel)
- mixer (stirrer)
- measurement and control system (acquisition of various parameters)
- dosing unit (valves and pumps)
- chemical reservoir (stock container) and
- concentrate reservoir (intermediate storage)

Cyanide and the parent compound hydrogen cyanide (HCN) are extremely toxic substances. The reason for the toxicity is that both substances form very stable aggregates with ferments (enzymes) of the human organism that contain heavy metals, so that the action of the ferments is inhibited. For this reason, it is absolutely essential that the cyanides are removed from the waste water. The aqueous solution of hydrogen cyanide is generally better known as prussic acid.

Decontamination of the cyanide-containing waste water takes place in partial reactions that are described below:

- oxidation of the cyanide to cyanogen chloride
- hydrolysis of the cyanogen chloride to cyanate
- oxidation of the cyanate to carbonic acid and nitrogen.

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Decontamination

As already explained at the beginning, the decontamination is carried out in continuous-flow treatment plants. Here, the waste water is first of all fed into the reactor. For the decontamination, a pH value of **at least** pH = 10 is required, and this is adjusted here. In the acid pH ranges, hydrogen cyanide is formed.

When sodium hypochlorite solution is added, the cyanide is converted to cyanogen chloride (ClCN) (reaction 1). Cyanogen chloride is a similarly toxic gas with a high solubility in water (25 liter ClCN gas/liter water).

In the next reaction stage, the cyanogen chloride is converted to the non-toxic cyanate (CNO-). This reaction only occurs at very high pH values. As the progress of the first partial reaction is not pH-dependent, the high pH value is adjusted right at the beginning of the decontamination. Generally, the total reaction is carried out with a 20% excess of NaOCl.

Under the conditions explained at the beginning, the decontamination is concluded within 20 minutes at most. However, the licensing authorities insist on durations of between 40 and 60 minutes, to ensure that all the cyanide was converted.

In the last section, the cyanate obtained above is oxidized to carbonic acid and nitrogen at pH values around 7-8. This reaction is completed within 30

minutes (reaction 3).

When the decontamination is completed, it is followed by further stages of neutralization, sedimentation, filter press and final inspection, before the purified waste water is fed into the sewer system.

Reaction 1	$2\ CN^- + 2\ OCl^- + 2\ H_2O \longrightarrow 2\ ClCN + 4\ OH^-$
	cyanogen chloride
Reaction 2	$2\ ClCN + 4\ OH^- \longrightarrow 2\ CNO^- + 2\ Cl^- + 2\ H_2O$
	cyanate
Reaction 3	$2\ CNO^- + 3\ OCl^- + H_2O \longrightarrow N_2 + 2\ CO_3^{2-} + 3\ Cl^- + 2\ H^+$

Chromate reduction

In the chromate reduction process, the toxic chromate ions are converted to chromium (III) ions. Chromate is produced in:

- ❏ electrolysis processes (lustrous and hard chrome)
- ❏ pickling and etching baths
- ❏ production of aluminum
- ❏ chrome-plating baths

Decontamination

Chromate is removed from the waste water in the acid range. Depending on the pH value, chromate (CrO_4^{2-}) forms in the alkaline range, and dichromate ($Cr_2\ O_7^{2-}$) in the acid range.

The pH value and the redox voltage are measured in the reactor. If the pH value is above 2.5, the pH value is adjusted to 2.5 with either dilute sulfuric acid or hydrochloric acid. A constant pH value is required for the quantitative conversion of the reaction. During the chromate decontamination, it must be ensured that no other acid waste water is fed into the plant.

The conversion of the toxic chromium (VI) compounds into chromium (III) compounds occurs in accordance with the following reaction equations:

$CrO_4^{2-} + 4\ H_2O + 3\ e^- \longrightarrow Cr(OH)_3 + 5\ OH^-$ (alkaline)

$Cr_2\ O_7^{2-} + 14\ H^+ + 6\ e^- \longrightarrow 2\ Cr_3+ + 7\ H_2O$ (acidic)

5.4 Power stations

In power stations, water is used for steam generation. To avoid dangerous deposits[3], the boiler water must be free from dissolved substances, the only presence permitted is an alkalizing agent such as ammonia. If the steam is collected and condensed, the condensate can be reused as boiler feed water. This condensate is almost like distilled water.

Pure water is very aggressive, particularly with a pH value below pH = 7. Corrosion damage can easily cost a small fortune. The problem here is that pure water also causes considerable problems with regard to the measurement. Even small impurities can appreciably affect the pH value, and taking a sample for a measurement is not really feasible. The pH measurement must be made in a through flow.

Measurement setup

Analysis of the vessel water is dealt with in the DVGW (German Gas and Water Association) specifications. Special measurement setups are required for pH measurement.

Contamination

All components of the measurement setup that come into contact with the water, fitting and flow-through cell, must be made of VA stainless steel. If plastic components are necessary, these must not give off any substances into the water. The electrode must contain a neutral electrolyte; a reference electrode containing silver chloride can react acidically, for example. The ideal arrangement is a dual electrode system, in which the reference electrode is mounted after the measuring electrode in the through flow. Because of the relatively high resistance of the water, an electrode with a low membrane resistance is recommended. The diaphragm should also have the lowest possible resistance, e.g. an annular diaphragm. With ceramic diaphragms, the resistance increases significantly as a result of water ingress. The electrolyte solution must be free of silver. The solubility of the silver chloride is rapidly reduced by contact with the electrolyte solution. Silver chloride deposits, which are difficult to dissolve, are formed in the diaphragm (the point of contact between the electrolyte and water).

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Boiler water has a conductivity below λ = 50 µS/cm, so that a normal pH transmitter is adequate for the measurement. The conductivity in condensate can be below λ = 1 µS/cm. In this case, a transmitter with a high-impedance input for the reference electrode is recommended. The measurement setup must be well grounded, so that electric charges can drain away.

[3] A coating on the boiler walls acts as thermal insulation and increases energy consumption. If part of the coating cracks, local overheating of the boiler water can occur, and, under certain circumstances, this can lead to a boiler explosion.

Flow

Every pH electrode reacts to the flow of the water. The lower the conductance and the higher the flow velocity, the more pronounced is this effect. The low conductivities of the boiler feed water and particularly the condensate can easily change the measured value by several tenths of a pH unit and even by up to one pH unit. Regulating the rate of flow in the measuring vessel is an effective measure here.

Alternative methods

As an alternative, it is possible to estimate the pH value of the water from the values for the conductivity or the ammonia content. However, the conductivity value only provides information on the maximum extent to which the pH value can deviate from the neutral point (pH = 7). It is impossible to make a statement on whether the water reacts acidically or basically, purely on the basis of the conductivity value.

Estimates based on the ammonia content can easily result in estimated pH values that are too high.

5.5 Drinking water supply systems

General

The pH measurement of the drinking water helps towards the hygiene and protection of the pipework system. The essential information provided by the pH value concerns the lime/carbonic acid equilibrium. The lime dissolved in the water exists in a state of chemical equilibrium with the dissolved carbon dioxide. The amounts of lime and carbon dioxide depend on the natural water used. If the water contains too little carbon dioxide, it deposits lime and forms a coating on the water feed pipe. If this condition persists over an extended period, the water pipe furs up. The critical factor is an excess of carbonic acid; it dissolves the lime coating. Without a protective coating, the pipeline material is exposed to corrosion. In the past, people have repeatedly suffered harm, and in extreme cases died, as a result of the release of heavy metals or the ingress of impure water.

Measurement setup

The optimal condition is when the pH value corresponds to the calcite saturation pH value. This is a value calculated from the composition of the water. If the pH value of the water corresponds to this value, there is neither lime deposition nor dissolving of the lime protective coating.

In accordance with the German drinking water regulations, the pH value must be in the range from pH = 6.5 to pH = 9.5. The calcite dissolving capacity (lime dissolving power) at the waterworks outlet must not exceed a value ss($CaCO_3$) = 5 mg/l; the requirement is deemed to be fulfilled if the pH value at the waterworks outlet exceeds pH = 7.7. With a mixture of water from two or more waterworks, the calcite dissolving capacity in the distribution system must not exceed the value of 20 mg/l.

The calcite dissolving capacity and the pH value for the lime/carbonic acid equilibrium are values that can be calculated from the composition of the water.

The pH measurement ensures that the pH value of the water corresponds to the calcite saturation pH value and that the pH = 7.7 value is exceeded. If the pH value is too low, the water must be treated using a suitable deacidizing process.

The drinking water regulations specify that the measurement method used for the pH measurement must have an accuracy of 0.2 pH units and a precision of 0.2 pH units.

When selecting an electrode, the parameters with most influence are: the water pressure, the flow velocity and the conductivity.

As contamination effects have no real significance, an electrode that has adequate pressure resistance, with reference electrolyte gel and a ceramic diaphragm, is suitable for this application.

A single-point calibration makes the normally time-consuming process of setting up and removal superfluous, conserves the measurement system and reduces the effect of the drinking water flow.

Comparison measurement

Pressure differences can be significant for the interpretation of comparison measurements. The effect of the carbon dioxide on the pH of the water also depends on the water pressure. This can easily be 6 bar and more in the pipeline. The higher the pressure, the more acidically the water reacts. If the pressure drops (for instance, when taking a sample) carbon dioxide will effervesce and the measured pH value will be increased.

5.6 Drinking water reservoirs

General

The outlay for drinking water treatment depends on the available natural water. Drinking water reservoirs or dams, for example, are a source of drinking water. The nature of the water in the supply system is normally very constant. In the reservoir, the weather itself can affect the condition of the water (long dry spell, heavy rainfall). A high supply of nutrients can lead to a massive development of phytoplankton (algae) within a few days. These can die again just as quickly. Storm water runoff can have an effect within a few hours. As a consequence, measurement setups that can provide information on the water condition, e.g. turbidity, oxygen content, pH value, electrical conductivity and water temperature, both quickly and without undue effort, are required for monitoring the reservoir.

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Measurement setup

There are no real problems with the measurement. Depending on the measurement point, a measurement setup with a immersion or flow-through fitting is adequate.

6 Other methods of pH measurement

6.1 Electrochemical methods

Antimony and bismuth electrode

Glass electrodes are extremely versatile. Special types of glass extend the range of use to cover the strong alkaline region or hydrofluoric acid solutions. Even so, limits are still imposed on this measurement technique. When the pH value is too low, hydrofluoric acid attacks even the best glass, and even a robust glass electrode does not achieve the reliability of a metal one. The antimony electrode can cover this range of extreme operating conditions. This electrode simply has a rod made of antimony metal. The potential formation occurs on the metal surface. However, with antimony, the equilibrium depends on the hydroxide ion activity, from which the hydrogen ion activity can be calculated, via the ionic product of the water.

Antimony electrodes are very robust, both mechanically and chemically. They are suitable for measurements in hydrofluoric acid or for monitoring in a lime solution precipitate.

The relationship between electric potential and pH value is not as linear as with a glass electrode. Antimony electrodes can be used in temperatures up to 80°C, in the range between pH = 1 and pH = 10. The system zero of an antimony electrode is around $pH_0 = 0 \pm 1.5$. The slope is normally in the range between k´= 51 mV and k´= 60 mV per pH.

In much the same way as the antimony electrode, the semimetal bismuth can also be used for pH measurements in the range between pH = 6 and pH = 10.

The transmitter for antimony and bismuth electrodes must be adjustable to the system zero, which deviates from that of the glass electrodes. The Jumo dTRANS pH01 transmitter, for example, is a suitable type in such a case.

ISFET

ISFET stands for **i**on **s**elective **f**ield **e**ffect **t**ransistor. These sensors differ not so much as a result of the membrane material but rather because of their construction.

For the high-impedance pH measurement with glass electrodes, a high-performance instrumentation amplifier (transistor) is required. Normal instruments have a resistance of at least $10^{12}\Omega$. One of the reasons for this is the high resistance of the glass membrane. The amplifier is often mounted in the instrument, in the fitting, or in a separate unit installed between the electrode and the instrument. The greater the distance between membrane and amplifier, the more sluggish and unresponsive is the signal transmission. With a long transmission path, each change in pH value means a time-consuming generation and movement of electric charges.

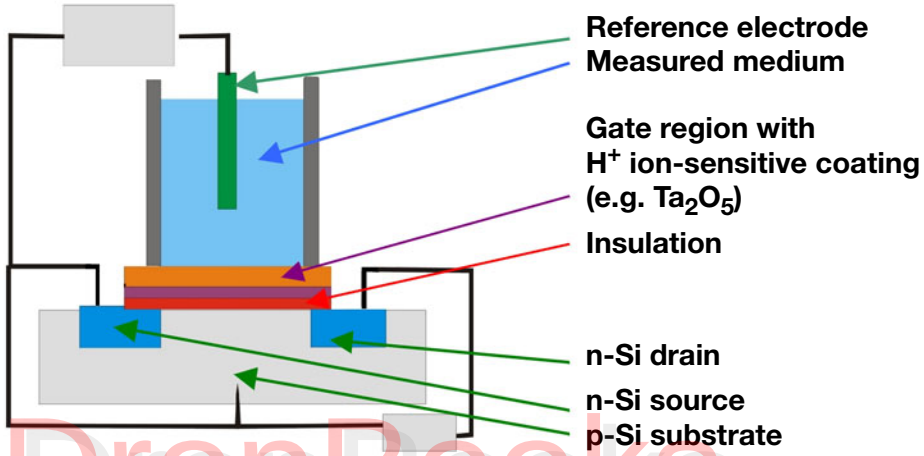

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Fig. ISFET sensor

With an ISFET sensor, the membrane forms a single unit with the amplifier. One advantage of this arrangement is the good response and reduced susceptibility to interference. As miniaturization of transistors does not present a problem, ISFET sensors are an interesting alternative in the field of biological and medical applications.

Depending on the membrane material, ISFET sensors have a limited range, worse linearity, shorter service live, reduced reliability, and are sensitive to light in some cases. These are without doubt some of the reasons why, until now, ISFET sensors have been used predominantly for operational measurements with hand-held instruments and for laboratory measurements in biology and medicine.

Finally, a reference electrode is also needed for pH measurement with ISFETs. This can be designed as a conventional reference system, which to some extent negates the ISFET's major advantage. Until now, other solutions using ISFET technology, known as REFETs (reference field effect transistor), have not demonstrated an adequate long-term stability.

6.2 Optical methods

Colorimetry

The simplest measurement setup consists of the sun (daylight) as a light source, a pH indicator, and the human eye. All that is required is to pour the water sample into a glass container (cuvette) and add an indicator solution to it. The indicator solution consists of a chemical substance that exhibits different colors depending on the pH value. The pH value can be easily determined by comparing the coloration with a color scale. It is a popular measurement method for individual measurements, e.g. in private swimming pools.

Colorimetry cannot satisfy demands for high accuracy. The measured value also depends on the level of daylight and the color-vision sensitivity of the user. Depending on the indicator, substances contained in the sample, or even just dissolved salts, can cause color adulterations. The range often only covers a narrow pH range.

Test stick

pH measurement with a test stick works in much the same way as the colorimetric method. The pH indicator is simply coated on to a plastic strip as a carrier. All that is required for the measurement is to dip the stick in the test solution and then determine the pH value by comparison with a color chart.

By using a combination of several indicators, some test sticks have really wide ranges. As well as the familiar problems with colorimetry, additional measurement deviations can occur as a result of the indicator bleeding. The pH indicator is therefore sometimes chemically bonded to the carrier material to avoid bleeding.

The uncertainties of the colorimetric method or the test stick are far greater than with electrochemical methods. Commercially available indicator sticks have a pH resolution of ΔpH = 0.5 or worse.

Photometry

The photometric pH measurement also works on the same principle as colorimetry. However, the measurement of the color intensity here is made with a photometer. These instruments contain a lamp as the light source and a silicon photocell as the light receiver. Photometric pH measurement gives more reproducible values than colorimetry. In addition, the resolution of the measured value is better as a result of the higher sensitivity of the light receiver. Measurement with a phenol red indicator is a measurement method widely used in the swimming pool sector.

7 Legal aspects

Waste-water treatment plants require official approval. This results in a whole list of duties for the operator of such a plant. Among others these include:

- ❏ the local authority's discharge licence must be available
- ❏ where new works or modifications to sections of existing plant are carried out, a new application for a discharge licence must be submitted
- ❏ prescribed limit values must be complied with
- ❏ if demanded, waste water must be tested and monitored in line with the requirements.
- ❏ The legal principles are laid down in appropriate EU Directives, federal and state laws and local authority regulations. The EU Directives listed in the overview will be incorporated into national law shortly or in the near future.

From the following list, it will be very clear that the planning, construction and commissioning of waste-water treatment plants is not an easy task, and that a multiplicity of clauses and regulations must be observed.

7.1 EU Directives

- ❏ 2000/60/EC Directive of the European Parliament and the Council establishing a framework for Community action in the field of water policy
- ❏ Order for amendment to the drinking water regulations, Article 1, Regulations governing the quality of water for human consumption (German drinking water regulations, 2001)
- ❏ 98/83/EC Directive on drinking water
- ❏ 91/271/EEC Treatment of urban waste water
- ❏ 87/217/EEC Prevention and reduction of environmental pollution by asbestos
- ❏ 86/280/EEC Directive on limit values and quality objectives for discharge of certain dangerous substances
- ❏ 84/491/EEC Directive on limit values and quality objectives for discharge of hexachlorocyclohexane (lindane)
- ❏ 84/156/EEC Directive on limit values and quality objectives for discharge of mercury by sectors other than the chlor-alkali electrolysis industry
- ❏ 83/513/EEC Directive on limit values and quality objectives for discharge of cadmium
- ❏ 82/176/EEC Directive on limit values and quality objectives for discharge of mercury by the chlor-alkali electrolysis industry
- ❏ 80/778/EEC Quality of water intended for human consumption
- ❏ 80/68/EEC Protection of groundwater against pollution
- ❏ 79/869/EEC Methods of measurement and frequency of sampling and analysis of surface water intended for the abstraction of drinking water

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- ❏ 76/464/EEC Water pollution by discharge of certain dangerous substances
- ❏ 76/160/EEC Quality of bathing water
- ❏ 75/440/EEC Quality of surface water intended for the abstraction of drinking water.

8 Closing remarks

All the points covered represent the current state of knowledge.

In view of the ongoing development of test and measurement methods, it is to be expected that new knowledge will be gained and put to practical use.

JUMO follows up developments in the world of standards, so as to be always up to date with the current state of technology and to be able to give you, our customer, access to the best possible measurement technology.

We are grateful for any suggestions you may have about this technical publication.

Our series of technical publications also includes:

- ❏ Information on high-purity water measurement
- ❏ Information on amperometric measurement of free chlorine, chlorine dioxide and ozone in water
- ❏ Information on redox voltage measurement

In addition, basic courses on different subjects and products take place throughout the year in our training center in Fulda. You can request a copy of the current seminar program by using the fax number +49 661 6003-682.

As well as the detailed description of the seminars, this also contains a list of the technical publications available.

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9 Source information

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